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[Amendments: There are no amendments attached to this patent. Translator's note]

[Note: All names, addresses, company names, and brand names are translated in the most common manner. Japanese language does not have singular or plural words unless otherwise specified with numeral prefix or general form of plurality suffix. Translator's note]

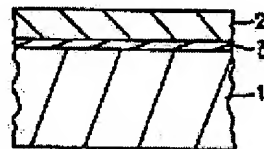
(54) [TITLE OF THE INVENTION]  
METHOD OF FORMING SOIL-RESISTANT LAYER [Bouqsoo no keiseihoho]

(57) [ABSTRACT]  
[SUBJECT]

Its purpose is to solve a subject on expressed crying toward formation of soil-resistance layer showing excellent soil resistance, scratch resistance, or solvent resistance and the like in a short time through a pretreatment on a surface of to-be treated base material such as various optical member parts and the like.

[MEANS OF SOLUTION]

This is the method to form a soil-resistant layer by using a soil-resistant agent on at the least one plane of a to-be treated base material, and offers a method to pre-treat at the least one plane of said to-be treated base material to form a stain-resistant layer on thus pre-treated surface prior to forming soil-resistant layer.



[Figure 1]

[CLAIMS]

[CLAIM ITEM 1]

A method that forms a soil-resistant layer by using a soil-resistant agent on at the least one plane of a to-be treated base material, wherein a method of forming said soil-resistant layer on a surface of pre-treated layer by pre-treating at the least one plane of said to-be treated base material prior to forming said soil-resistant layer.

[CLAIM ITEM 2]

The method of forming soil-resistant layer according to the claim item 1, wherein said pre-treatment is of any by a high frequency discharge plasma method, an electron beam method, an ion beam method, a vapor deposition method, a sputtering method, an alkali treatment method, an acid treatment method, a corona treatment method, or atmospheric pressure glow discharge plasma method.

[CLAIM ITEM 3]

The method of forming soil-resistant method according to the claim item 1 or claim item 2, wherein said to-be treated base material is of optical member part.

[CLAIM ITEM 4]

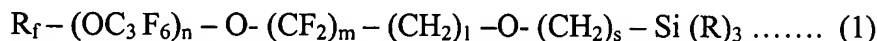
The method of forming soil-resistant layer according to the claim item 3, wherein said optical member part is any of optical lens, spectacle lens, camera or binocular, or lens beam splitter, prism, mirror, window glass, anti-reflective film, or optical filter of other optical devices.

[CLAIM ITEM 5]

The method of forming soil-resistant layer according to any of claim items 1 ~ 4, wherein said anti-stain agent is organic silane compounds that include perfluoro polyether group.

[CLAIM ITEM 6]

The method of forming soil-resistant layer according to any of claim items 1 ~ 5, wherein said anti-stain agent comprises organic silane compound shown with general formula (1).



(However,  $R_f$  shows either straight-chain form or branch-form perfluoro alkyl group with 1 ~ 16 number of carbon atoms, and  $n$  shows 1 ~ 50 integers, and  $m$  shows 0 ~ 3 integers, and  $l$  shows 0 ~ 3 integers, and  $s$  shows 0 ~ 6 integers; however, it is  $6 \geq m+1 > 0$ , and  $R$  shows hydrolysis group.)

[CLAIM ITEM 7]

The method of forming soil-resistant layer according to any of claim items 1 ~ 6, wherein said soil-resistant agent is heated to evaporate under 1 Pa or lower pressure to film form on a to-be treated base material.

[CLAIM ITEM 8]

The method of forming soil-resistant layer according to any of claim items 1 ~ 7, wherein heating method for purpose of evaporation of said soil-resistant agent is of a resistant heating method, an electron beam heating method, a light heating method, an ion beam heating method, or a high frequency heating method.

[CLASIM ITEM 9]

A manufacturing method of optical member [art having soil-resistant layer is characterized by the fact that form said soil-resistant layer in accordance with the methods described in any of claim items 3 ~ 8.

[CLAIM ITEM 10]

An optical member part having soil-resistant layer is characterized by the fact that at the least one plane of optical member part is pre-treated.

[CLAIM ITEM 11]

The optical member part having soil-resistant layer according to the claim item 10, wherein optical member part is any of optical lens, spectacle lens, camera or binocular, or lens, beam splitter, prism, mirror, window glass, anti-reflective film, or optical filer of other optical devices.

[CLAIM ITEM 12]

The optical member part having soil-resistant layer according to any claim item of 10 ~ 11, wherein said soil-resistant agent is organic silane compound that includes perfluoro polyether group.

[CLAIM ITEM 13]

The optical member part having sol-resistant layer according to any claim items 10 ~ 12, wherein said soil-resistant agent comprises organic silane compound with a general formula (1).



(However,  $R_f$  shows either straight-chain form or branch-form perfluoro alkyl group with 1 ~ 16 number of carbon atoms, and  $n$  shows 1 ~ 50 integers, and  $m$  shows 0 ~ 3 integers, and  $l$  shows 0 ~ 3 integers, and  $s$  shows 0 ~ 6 integers; however, it is  $6 \geq m+1 > 0$ , and  $R$  shows hydrolysis group.)

## [DETAILED EXPLANATION OF THE INVENTION]

[0001]

### [APPLICABLE FIELDS]

This invention relates to the method of forming soil-resistant layer on a surface of various to-be treated base materials requiring soil resistance. In further detail, this invention relates to the method to promptly fix soil-resistance layer on various to-be treated base materials.

[0002]

### [PRIOR ART]

An anti-reflection treatment is generally applied to surfaces of optical lens, spectacle lens, lens of camera or binocular in order to reduce reflection of lights and to enhance transmission of lights. There are many cases when soil such as finger prints, sebaceous matter, perspiration, or cosmetics and the like through use of these optical member parts by men.

[0003]

In general, due to a large surface energy such as of about  $60 \text{ J/m}^2$  of anti-reflective film, soil tends to become adhered, and furthermore, it is not easy to remove this due to micro-size unevenness [concave, convex]. In addition, it has been known to present such problems as only the portion where such soil is adhered shows high reflection allowing such soil to be noticeable.

[0004]

As means of solving these soil problems, means to arrange a soil-resistant layer showing such performance as difficult adhesion of soil, and an easy wipe off property in a case of adhesion by that [said soil] has been designed.

[0005]

For instance, according to the Japanese patent application of Kokai [laid-open] Sho 64 [1989]-86101 publication, anti-reflective film goods showing soil resistance as well as scratch resistance through arrangement of a anti-reflective film on a surface of base material in addition to further treatment on that surface with a compound that includes organic silicon substituent has been proposed.

[0006]

According to the Japanese patent application of Kokai [laid-open] Hei 4 [1992]-338901 publication, a CRT filter showing soil resistance and scratch resistance of which base material surface is covered with a film of organic polysiloxane with terminal silanol in the same manner as explained above has been proposed.

[0007]

Furthermore, according to the Japanese patent application of Kokoku [post-examined] Hei 6 [1994]-29332 publication, a plastic showing low reflective index and soil resistance that has an anti-reflective film on its surface of which said anti-reflective film comprises mono and disilane compound having polyfluoro alkyl group and silane compound of halogen, alkyl, or alkoxy has been proposed.

[0008]

In addition, according to the Japanese patent application of Kokai [laid-open] Hei 7 [1995]-16940 publication, an optical goods on which optical thin film having main component of silicon dioxide, a copolymer of perfluoro alkyl (meth)acrylate and a monomer having alkoxy silane group has been proposed.

[0009]

[SUBJECTS SOLVES BY THIS INVENTION]

However, according to conventional technologies of forming soil-resistant layers, they require long time of several house, or in some cases, several days until soil resistance, wear resistance, or solvent resistance and the like becomes maximum after film forming of soil-resistant layer, and problems such as soil or scratches are easy to occur during such time, and furthermore part of soil-resistant layer is transferred when it comes in contact with other goods to allow peeling of soil-resistant layer have been pointed out.

[0010]

This invention sets out to solve above-explained subjects of prior art; and purpose of this invention is to offer the method of forming soil-resistant layer that can form soil-resistant layer showing excellent soil resistance, scratch resistance, solvent resistance and the like in short time through pretreatment on the surface to to-be treated base material such as various optical member parts.

[0011]

[MEANS USED TO SOLVE THE SUBJECTS]

According to the first claim of this invention, it solves said subjects through a method that forms soil-resistance layer that is characterized by using a soil-resistant agent on at the least one plane of to-be treated base material; and prior to forming said soil-resistant layer, at the least one plane of said to-be treated base material is pretreated, and soil-resistant layer is film formed on the surface that has been pretreated.

[0012]

According to the second claim of this invention, it relates to the method of forming soil-resistant layer that is described in the claim item 1, wherein uses any methods such as a high frequency discharge plasma method, an electron beam method, an ion beam method, a vapor deposition method, a sputtering method, an alkali treatment method, an acid treatment method, a corona treatment method, or atmospheric pressure glow discharge plasma method.

[0013]

According to the third claim of this invention, it relates to the method of forming soil-resistant layer that is described in either claim item 1 or claim item 2, wherein said to-be treated base material is optical member parts.

[0014]

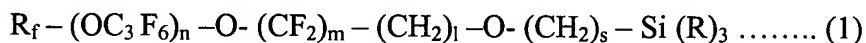
According to the fourth claim of this invention, it relates to the method of forming soil-resistant layer that is described in the claim item 3, wherein optical member parts are any one of optical lens, spectacle lens, camera or binocular, or lens, beam splitter, prism, mirror, window glass, anti-reflective film, and optical filter of other optical devices.

[0015]

According to the fifth claim of this invention, it relates to the method of forming soil-resistant layer that is described in any of claim items 1 ~ 4, wherein soil-resistant agent for film forming of said soil-resistant layer is organic silane compound that includes perfluoro polyether group.

[0016]

According to the sixth claim of this invention, it relates to the method of forming soil-resistant layer that is described in any of claim items 1 ~ 5, wherein said soil-resistant agent comprises organic silane compound shown with a general formula (1).



(However,  $R_f$  shows either straight-chain form or branch-form perfluoro alkyl group with 1 ~ 16 number of carbon atoms, and  $n$  shows 1 ~ 5- integers, and  $m$  shows 0~ 3 integers, and  $l$  shows 0 ~ 3 integers, and  $s$  shows 0 ~ 6 integers; however, it is  $6 \geq m+1 > 0$ , and  $R$  shows hydrolysis group.)

[0017]

According to the seventh claim of this invention, it relates to the method of forming soil-resistant layer that is described in any of claim items 1 ~ 6, wherein said soil-resistant agent is heated to evaporate in a vacuum to film form on a to-be treated base material.

[0018]

According to the eighth claim of this invention, it relates to the method of forming soil-resistant layer that is described in any of claim items 1 ~ 7, wherein heating method for purpose of evaporating said soil-resistant agent is a resistant heating method, an electron beam heating method, a light heating method, an ion beam heating method, or a high frequency heating method.

[0019]

According to the ninth claim of this invention, it relates to a manufacturing method of optical member part having soil-resistant layer that is characterized by the fact that forms said soil-resistance layer through any methods described in the claim items 3~ 8.

[0020]

According to the tenth claim of this invention, it relates to the optical member [art having soil-resistant layer that is characterized by the fact that at the least one plane of optical member part has a surface that is pretreated.

[0021]

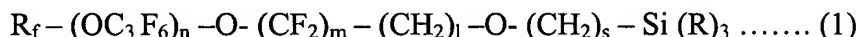
According to the eleventh claim of this invention, it relates to the optical member part having soil-resistant layer that is described in the claim item 10, wherein optical member part is optical lens, spectacle lens, camera or binocular, or lens beam splitter, prism, mirror, window glass, anti-reflective film, or optical filter of other optical devices.

[0022]

According to the twelfth claim of this invention, it relates to the optical member part having soil-resistant layer that is described in claim items 10 ~ 11, wherein said soil-resistant agent is organic silane compound that includes perfluoro polyether group.

[0023]

According to the thirteenth claim of this invention, it relates to the optical member [art having soil-resistant layer that is described in any claim items of 10 ~12, wherein said soil-resistant agent comprises organic silane compound that is shown with general formula (1).



(However,  $R_f$  shows either straight-chain form or branch-form perfluoro alkyl group with 1 ~ 16 number of carbon atoms, and  $n$  shows 1 ~ 50 integers, and  $m$  shows 0 ~ 3 integers, and  $l$  shows 0 ~ 3 integers, and  $s$  shows 0 ~6 integers; however, it is  $6 \geq m+1 >0$ , and  $R$  shows hydrolysis group.)

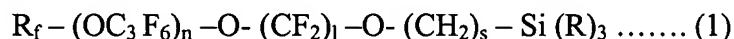
[0024]

#### [IMPLEMENTATION FORMAT OF THIS INVENTION]

This invention is explained in details.

[0015]

When film forming a soil-resistant layer on a to-be treated base material, soil-resistant agent comprising organic silane compound that includes perfluoro polyether group is used. Regarding said organic silane compound, compounds or its polymers shown with general formula (1) are suitable.





[0026]

In general, according to the general formula (1),  $R_f$  shows either straight chain-form or branch-form perfluoro alkyl group with 1 ~ 16 number of carbon atoms; and in particular,  $CF_3-$ ,  $C_2F_5-$ , and  $C_3F_7-$  are recommended.  $R$  shows hydrolysis group, and  $-Cl$ ,  $-Br$ ,  $-I$ ,  $-OR^1$ ,  $-OOCR^1$ ,  $-OC(R^1)C=C(R^2)_2$ ,  $-ON=C(R^1)_2$ ,  $-ON=CR^3$ ,  $-N(R^2)_2$ , or  $-R^2NOCR^1$  and the like are recommended.

[0027]

However,  $R^1$  shows aliphatic hydrocarbon group with 1 ~ 10 number of carbon atoms such as alkyl group and the like, or aromatic hydrocarbon group with 6 ~ 20 number of carbon atoms such as phenyl group; and  $R^2$  shows aliphatic hydrocarbon group with 1 ~ 5 number of carbon atoms such as hydrogen atom or alkyl group and the like; and  $R^3$  shows divalent aliphatic hydrocarbon group with 3 ~ 6 number of carbon atoms such as alkylidene [transliteration] group and the like.

[0028]

Regarding hydrolysis group in above-explained organic silane compound, it is all right to use not only one type but also a mixture system of more than two types. In particular,  $-OCH_3$ ,  $-OC_2H_5$ ,  $-OOCCH_3$ , or  $-NH_2$  are recommended. Furthermore,  $n$  shows 1 ~ 50 integers; and  $m$  shows 0 ~ 3 integers, and  $l$  shows 0 ~ 3 integers; and  $s$  shows 0 ~ 6 integers, however, it is  $6 \geq m+1 > 0$ .

[0029]

It is preferable when PVD method that does not use diluted solvent is used at the time of forming of soil-resistant layer from the standpoint of work environment or control over film thickness; and in particular, it is preferable when it is done by a vacuum vapor deposition method. According to said method, said soil-resistant agent is heated under the pressure of 1 Pa or lower to evaporate to form on a to-be treated base material.

[0030]

Regarding heating method, methods such as a resistance heating method, an electron beam heating method, a light heating method, an ion beam heating method or a high frequency heating method are effective. According to PVD method, it is possible to control film thickness of soil-resistant layer to the order of Angstrom that has been considered difficult by a conventional method.

[0031]

Regarding soil-resistant agent that include organic silane compound explained above is considered to initiate a hydrolysis through reaction of OH group on the to-be treated base material surface and hydrolysable group of organic silane compound to form a chemical bonding. However, hydrolysis reaction between soil-resistant layer and to-be treated base material surface is generally slow, and it requires such time of several hours to several tens of days from the time said soil-resistant layer is totally fixed to display maximum soil resistance, scratch resistance or solvent resistance and the like.

[0032]

On the one hand, according to this invention's pretreatment methods such as a high frequency discharge plasma method, an electron beam method, an ion beam method, a vapor deposition method, a sputtering method, an alkali treatment method, an acid treatment method, corona treatment method, or atmospheric pressure glow discharge plasma method and the like, they can form to-be treated base material surface to which soil-resistant layer comprising soil-resistant agent that includes organic silane compound is easily fixed because it not only cleans to-be treated base material surface but also isolate molecular bonding on the surface to create an active surface.

[0033]

Said to-be treated base material is particularly effective on optical lens, spectacle lens, camera or binocular, lens, beam splitter, prism, mirror, window glass, anti-reflective film, or optical filter and the like of other optical devices.

[0034]

[EXAMPLES]

This invention's examples are explained below, however, it should not be limited to these.

[0035]

<EXAMPLE 1>

An anti-reflective film is placed within a parallel flat plate-type high frequency discharge device; and inside of this device was exhausted to  $1.0 \times 10^{-3}$  Pa. Hydrogen gas was introduced to said device at 10 sccm/min flow rate, and pressure was adjusted to  $1.0 \times 10^{-1}$  Pa. High frequency (frequency = 13.56 MHz) was applied to said device, and said anti-reflective film was exposed to thus generated 100W plasma for 1 minute to carry out pretreatment on the surface of said anti-reflective film.

[0036]

Then, organic silane compound shown with general formula (2) was placed on a molybdenum boat, and soil-resistance layer was formed on said anti-reflective film by a vacuum vapor deposition method (resistance heating method). After exhausting inside of vacuum vapor deposition device to  $1.0 \times 10^{-3}$  Pa or lower, boat was heated to 400°C to evaporate said organic silane compound.



[0037]

<EXAMPLE 2>

Surface of anti-reflective film was pretreated by exposing to 50 W/m<sup>2</sup>.min corona discharge generated in atmospheric pressure. Then, soil-resistance layer was formed on said anti-reflective film in the same manner as explained in the example 1.

[0038]

<COMPARATIVE EXAMPEL 1>

Said organic silane compound was used to form soil-resistant layer on an anti-reflective film that was not subjected to the pretreatment in the same manner as explained in the example 1. Various physical property evaluation methods and results conducted on above-explained examples 1 and 2 and comparative example are shown in the (Table 1) below.

[0039]

(a) CONTACT ANGLE MEASUREMENT:

Contact angle gauge [CA-X type: made by Kyowa Kaimen Kagaku K.K.] was used to form a droplet with 1.0 mm diameter in a dry state (20°C -65%RH) on a needle tip; and this was contacted with a surface of base material (solid object) to form a droplet. Contact angle refers to the angle that is formed by a contact line against liquid surface at the point where solid liquid is in contact and solid surface; and it is defined as the angle on the side that includes liquid. As for the liquid, distilled water was used.

[0040]

(b) WEAR RESISTANCE:

Said physical property was evaluated after rubbing base material with cellulose made nonwoven cloth [Bencot M-3 [transliteration]: made by Asahi Kasei K.K.] for 100 times under 500 gf/m<sup>2</sup> load.

[0041]

[Table 1]

	Contact angle measurement (°)		
	Immediately after film forming	10 hours after film forming	After wear resistance test
Example 1	114.5	114.8	113.5
Example 2	113.8	114.5	113.1
Comparative example 1	95.1	114.1	100.3

[0042]

[EFFECTS OF THIS INVENTION]

According to the method of this invention, it becomes possible to form a soil-resistant layer with high fixing property and durability and shows such performance of difficult for soil such as finger prints, sebaceous matter, perspiration, or cosmetics and the like to adhere as well as easy wipe off even when such adhesion takes place without ill-affecting various optical characteristics on various optical member parts (optical lens, spectacle lens, camera or binocular, or lens, beam splitter, prism, mirror, window glass, anti-reflective film, optical filter of other optical devices).

[BRIEF DESCRIPTION OF THE FIGURES]

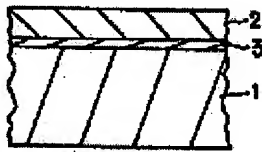
[FIGURE 1]

It illustrates a cross sectional view of optical member part of this invention.

[DESCRIPTION OF CODES]

- 1 transparent base material
- 2 soil-resistant layer
- 3 treated plane

[Figure 1]



Translation requested by: Virginia Bergstrom for Jean Lown and Pam Stewart OIPC  
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